

APPENDIX A

Small Stream Toxicity Study

Sampling and Analysis Plan

Name of Project: SMALL STREAMS TOXICITY STUDY

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APPROVED BY

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1.0 PROJECT DESCRIPTION

Background

The United States Geological Survey (USGS) and the Washington Department of Ecology (Ecology) have been studying the ambient distribution of pesticides in the Puget Sound Region for much of this decade under the National Water Quality Assessment Program (NAWQA). Much of this work has involved storm sampling, in effect monitoring current trends in non-point pollution. Initial findings focused subsequent efforts on small suburban streams. The highest number of pesticide detections have occurred in the urban/suburban setting, particularly in watersheds with a high percentage of residential land use. This has led to the conclusion that chemicals from lawns and landscapes are consistently making their way into non-point run off.

In the spring of 1998 King County collaborated with the USGS and Ecology to test for toxicity in Lyon Creek, a small stream located in Lake Forest Park. This testing was conducted alongside the USGS / Ecology pesticides testing. Chronic toxicity was detected for both the algae *Selenastrum* and the water flea *Daphnia* in this sample. These detections violate State Water Quality Standards and are suspected to be linked to pesticides present in the sample.

1999 Sampling and Testing

The Small Streams Toxicity Study is being conducted to further investigate the prevalence and possible causes of toxicity in small streams. Samples will be collected in four sampling events during four seasons: spring, summer, fall, and late fall. All but summer will be storm events. All samples will be analyzed for toxicity, pesticides, total suspended solids, and metals. In addition, selected sites will be tested for Base/Neutral/Acid (BNA) compounds, a standard list of organic pollutants.

The sale of lawn care products peaks in the spring, with a secondary peak in the fall. The timing of the sampling events is selected with this in mind. Three test sites will be selected for Spring and Two test sites for Summer, Fall, and Winter. A reference site will be included for each sampling event/season.

Sites are selected based on previous pesticide data. Site selection is intentionally biased towards the most contaminated (pesticides) sites, to increase the probability of detecting toxicity and other pollutants that may be present. One site with previously low detected pesticides has also been selected as a point of comparison. A reference site will also be sampled.

Data will primarily be used to determine the prevalence of toxicity at these suburban stream sites. A secondary use of the data will be to compare toxicity detection with the presence of chemical pollutants and gain further insight as to the possible cause(s) of detected toxicity.

The results may be used to guide further studies of this nature.

2.0 PROJECT ORGANIZATION AND RESPONSIBILITY

Name	Affiliation	Role
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3.0 DATA QUALITY OBJECTIVES

The procedures and practices described in this Sampling and Analysis Plan are designed to generate data of the type and quality necessary to support decision making as discussed in the project description section. Critical elements of data quality objectives are discussed in this section. Procedures to attain these data quality objectives are discussed throughout this document.

An associated QA Plan has not been prepared for this project. However, additions such as data reporting have been made to this SAP to include some of the topics normally included in a project QA Plan.

Precision and Bias

Laboratory default QC procedures are sufficient for both the chemical testing and toxicity testing. Replicates, positive and negative control samples as per routine laboratory protocol are to be analyzed for this study. A reference site is included in each sampling event.

All organics (pesticides, herbicide and BNA) analyses are to include surrogate compounds.

Some pesticide compounds are present on both the USGS and Ecology target lists, analytical replicate data will be available for these compounds. However, it should be pointed out that only USGS will filter pesticide samples prior to analysis.

At least one field replicate will be collected for metals and pesticides/herbicides in the early phases of the study, either the spring or summer sampling.

Elements of “clean hands” sampling will be employed to prevent contamination of metals samples. A field blank will be collected for metals during each sampling event. Metals results will be compared to water quality standards.

Representativeness

Sites to be sampled are not considered to represent all such sites in this region. Selected high bias sites have higher levels/and or more detections of pesticides than other sites studied. A site with low previous detected levels of pesticides, a low bias site, has also been selected.

The timing of the sampling event is selected to enhance the probability of detecting pollutants and toxicity. Storm water samples will be collected as stream levels rise during the initial runoff from a storm event.

Pesticide, toxicity, BNA, and total suspended solid samples will be collected using a technique which collects a representative grab sample. This technique composites a group of grab samples taken across a stream cross section. Metals samples will be

collected from a single high flow location within the stream. This is considered to approximate representative sampling techniques. It should be pointed out that for some parameters, such as the low levels metals analysis, the likelihood of contamination from a multiple sample compositing technique far outweighs the possible advantages of obtaining a slightly more representative sample.

Comparability

Sampling technique is coordinated with USGS and employs the same technique as in previous studies for the toxicity and pesticide samples. Other parameters have not previously been sampled and tested.

Labs used for previous studies are to be used for this study as well. This enhances data comparability.

Completeness

Based on data usage, and the limited and focused nature of this study, all parameters are needed for each site except BNA compounds, which will be sampled twice. Analytical difficulties are to be relayed to the Project Manager, Dean Wilson. In this event, he will coordinate with other data users, George Perry and Jim Ebbert, to formulate a potential resolution.

Hold times are to be met for all analyses.

Detection limits are not expected to vary significantly from those contained in the attachment to this SAP.

4.0 SAMPLING PROCEDURES

The following table summarizes sample collection and analysis.

Sampling Summary Table

Site	Spring Runoff	Summer Baseflow	Early Fall Runoff	Late Fall Runoff
Lyon Creek (high bias site)	Toxicity, Pesticides, Metals, TSS and BNAs	Toxicity, Pesticides, Metals, TSS and BNAs	Toxicity, Pesticides, TSS, and Metals	Toxicity, Pesticides, TSS, and Metals
Juanita Creek (high bias site)	Toxicity, Pesticides, TSS, and Metals	Toxicity, Pesticides, TSS, and Metals	Toxicity, Pesticides, TSS, and Metals	Toxicity, Pesticides, TSS, and Metals
Lewis Creek (low bias site)	Toxicity, Pesticides, TSS, and Metals	No sampling planned	No sampling planned	No sampling planned
Rock Creek Reference Site	Toxicity, Pesticides, TSS, and Metals	Toxicity, Pesticides, TSS, and Metals	Toxicity, Pesticides, TSS, and Metals	Toxicity, Pesticides, TSS, and Metals

Additionally, field blanks and replicates will be collected for selected parameters as summarized in the field QC table.

Storm sampling will commence when a storm of a high enough magnitude occurs and causes visible stream turbidity. The ideal storm would occur after a weekend of good

weather. Weather predictions and telemetering devices in the Lyon Creek basin that measure rainfall and stream flow will be used to aid in determining when to mobilize and sample.

Three sampling teams will be formed. Two of the sampling teams will sample the four creeks in the spring with each team being responsible for two creeks. The third sampling team will conduct the field extractions. The extraction team will be centrally located to expedite sample transfer from the sampling teams.

Filtration

Filtration will be conducted in the field for USGS Method 2010 as described below. Filters are to be stored frozen in glass jars until permission for disposal is granted by the project manager. Any filtering conducted for toxicity testing will be conducted by the aquatic toxicity laboratory. Filters may be discarded.

Pesticides/Toxicity/BNATSS

Samples representative of the flow in the stream cross section will be obtained by collecting depth-integrated subsamples at equally spaced verticals across the stream using either the US DH- 81 or US D-77 sampler as described by Edwards and Glysson (1988) and Shelton (1994). Both samplers hold a 3-liter Teflon sample bottle, and all parts of the sampler coming into contact with sample water are constructed of Teflon. Samples will be composited in a glass carboy in order to integrate the stream cross section. A Teflon cone splitter will be used to split the composited sample into various subsamples needed for laboratory analyses. All equipment used to collect and process samples will be cleaned with a 0.2-percent non-phosphate detergent, rinsed with deionized water, and rinsed with pesticide-grade methanol.

Pesticide samples to be analyzed by the USGS will be filtered through a 0.7 micrometer (μm) glass-fiber filter and field-extracted from the filtrate by pumping the filtrate through C-18 solid-phase extraction (SPE) cartridges. Detailed descriptions of equipment required and the procedures used to collect, process, and extract the sample using the SPE method are given in Shelton (1994). Pesticide samples to be analyzed by the WDOE laboratory will not be filtered. All samples, whether extracted or not, will be stored on ice and delivered to the pesticide analysis laboratories within 48 hours of sample collection.

Field Blank. Field blanks will be collected for pesticide testing. Clean water will be used in field blank collection. Laboratory water will be drawn through the stream sampler (described above), into the sample bottles and then into the compositing carboy. The Teflon cone splitter will be used to split a sample aliquot into a sample bottle for blank testing.

Field Replicate. To assess the precision of the field sampling and analytical processes, one (1) field replicate sample will be collected at a given site.

Metals

A modified EPA Method 1669 approach has been developed for collection of low-level metals samples. It is critical that any object or substance that contacts the sample is non-metallic and free from any material that may contain metals of concern.

Equipment/Definition:

- Gloves – clean, non-talc polyethylene, latex, vinyl, or PVC
- Storage Bags – clean, zip-type, non-vented, colorless polyethylene
- Cooler – clean, non-metallic, with white interior
- Reagent water – water in which the analytes of interest and potentially interfering substances are not detected at the Method Detection Limit (MDL) of the analytical method used for analysis of samples.

An acid washed polyethylene 500-ml bottle will be double bagged in ziplock type bags. Sampling personnel are required to wear clean, non-talc gloves at all times when handling sampling equipment and sample containers.

Sample Collection Procedures:

The sampling team should approach the site from down current and downwind to prevent contamination of the sample by particles sloughing off the vehicle or equipment. If it is not possible to approach from downwind, the site should be approached from down current.

Once at the sample site, withdraw the ziplock bag containing the appropriate metals bottle. Unzip the outer bag. Next, put on a pair of clean gloves and open the inside bag containing the sample bottle. Remove the bottle, and reseal the inside bag. Facing upstream, preferably in the portion of the channel with predominant flow, unscrew the cap. While holding the cap upside down, invert and submerge the sample bottle, and allow the bottle to partially fill with sample. Screw the cap on the bottle and shake the bottle several times. Empty the rinsate downstream of the sample site. Avoid stirring up the sediment as this can change the test results drastically. After two more rinsings, hold the bottle under water and allow the bottle to fill with sample. After the bottle has filled, and while the bottle is still inverted so that the mouth of the bottle is underwater, replace the cap of the bottle. In this way, the sample will not contact the air.

Reopen the inside bag and place the bottle inside it. Reseal all ziplock bags and place the package inside the cooler.

A new set of gloves must be used for each sample.

Field QC Sampling Procedure for Metals:

Field Blank. To demonstrate that sample contamination has not occurred during field sampling and sample processing one (1) field blank must be generated. Field blanks are collected **before** sample collection.

A clean acid washed one liter bottle will be filled with reagent water in the laboratory, double bagged, and brought to the field for “collection”. At the field collection site, the container will be removed from the bags as described above. Rinse an empty sample container, which has also been double bagged three times with the reagent water and then fill and cap the bottle. The field blank will be re-bagged and place in the cooler with the other samples.

Field Replicate. To assess the precision of the field sampling and analytical processes, at least one (1) field replicate sample must be collected at a given site. The field duplicate is collected by collecting two samples in rapid succession at the same site.

Sample Identification

Each sample will be identified by a unique laboratory sample number, assigned to each sampling location and event. A single sample number will be used for all parameters analyzed from the same sample. Sample numbers will be assigned and sample containers labeled with these sample numbers prior to use in the field. Sample labels will also include information about the sampling location, sampling date, project number, sample matrix, requested analytical parameters and preservative.

KCEL sample identification numbers will be assigned for all samples and will be used as a cross reference for samples going to the Ecology and USGS laboratories. KCEL labels will be provided for Ecology and USGS samples.

Sample Containers

All sample containers for samples to be analyzed at the KCEL will be supplied by the KCEL. These containers will be prewashed and prepared for sampling in accordance with standard operating practice of the KCEL.

Sample containers for samples to be analyzed at the USGS Laboratory will be supplied by the USGS. Sample containers for samples analyzed at the Ecology Manchester Laboratory will be obtained from Ecology.

Sample Containers, Preservation and Storage Conditions

Parameter	Matrix	Sampling Container	Container Size	Preservative	Hold Time
USGS schedule 2010 pesticides	water	Teflon	3L		?
Ecology chlorinated organophosphorus and nitrogen-containing pesticides	water	Amber glass	1 gallon	4°C	7 days to extract, 40 days to analyze
Ecology Chlorinated Herbicides	water	Amber glass	1 gallon	4°C	7 days to extract, 40 days to analyze
KCEL total Metals	water	Polyethylene (acid rinsed)	500ml	At lab, HNO ₃ to a pH less than 2	180 days 28 days Hg
KCEL BNA	water	Amber glass with Teflon® lid	Three, 1-Liter	4°C	7 days to extract 40 days to analyze
KCEL Toxicity	water	glass	3 each 2-L	4°C	36 hours
Filters	0.45 micron from toxicity testing			freeze	
Filters	0.7 micron, from USGS testing			freeze	
TSS	water	polyethylene	1 L	4° C	7 days

Sample Preservation

Samples will be preserved in accordance with the guidelines and references listed in the above table.

Samples will be preserved as soon as possible after sample collection and always within 24 hours of sampling. After collection, all samples will immediately be placed in an ice-filled, insulated cooler to maintain sample temperature of approximately 4°C until delivery to the laboratory.

Sample Delivery

All samples will be delivered to the various laboratories in sufficient time to allow the laboratories to meet the analytical hold times specified in the table above. Additionally, sample preservation requirements note that samples are to be preserved within 24 hours of sampling.

Samples will be carried by USGS to the National Water Quality laboratory for USGS schedule 2010 analyses, and to Ecology's Manchester Laboratory for chlorinated pesticides, organophosphorus pesticides, chlorinated herbicides, and nitrogen-containing pesticides analyses.

Metals samples must be delivered to the KCEL in sufficient time to allow for sample preservation within 24 hours.

Chain of Custody

The Chain of Custody forms to be used for this project are included as attachments to this QA plan. The USGS will handle chain of custody for samples delivered to the USGS Laboratory. The KCEL Chain of Custody form, or *Laboratory Work Order* form should be initiated in the field as samples are collected and accompany all samples during transport to the laboratory.

The sample release section of the chain-of-custody form is completed at the time of sample transfer to the laboratory. Date and time of sample delivery as well as the signature of the individual delivering the samples (Relinquished By) must be filled out at this time. The sample recipient (Received By) completes the chain-of-custody form and provides a copy to the sample deliverer.

At each sampling location, the following information will be recorded on waterproof field notes: date and time of sample collection, sampling personnel, station location information, weather conditions, number and type of samples collected, any unusual ambient conditions, and any deviations from sampling procedures specified in this document. If field measurements are collected or field analyses performed, results are also recorded on the field notes.

Field Quality Control Samples

Parameter	Field QC Sample Type	Frequency
Total Metals (includes Hg)	Field Blank	Once per Event
Total Metals (includes Hg)	Field Replicate	Once per Project
Pesticides	Field Blank	Twice per Project
Pesticides	Field Replicate	Once per Project

5.0 ANALYTICAL PROCEDURES - SUMMARY OF TESTING

A summary of the testing to be conducted for this site is listed below;

Laboratory Analysis Summary

Parameter	Matrix	Number of Samples	Method	LABORATORY
Organochlorine Pesticides	Water	16	US EPA 8085***	Washington Department of Ecology
Chlorophenoxy Herbicides	Water	16	US EPA 8085	Washington Department of Ecology
Organophosphorus Pesticides	Water	16	US EPA 8085	Washington Department of Ecology
Nitrogen Pesticides	Water	16	US EPA 8085	Washington Department of Ecology
Miscellaneous Pesticides	Water*	16	USGS 2010	US Geological Survey
Total Metals	Water	18	EPA 200.8	King County Environmental Laboratory
BNA	Water	2	SW 846-8270	King County Environmental Laboratory
<i>Ceriodaphnia</i> Chronic Toxicity	Water**	13	EPA 600/4-89/001	King County Environmental Laboratory
<i>Selenastrum</i> Chronic Toxicity	Water**	13	EPA 600/4-89/001	King County Environmental Laboratory
Total Suspended Solids	Water	13	SM 2540-D	King County Environmental Laboratory

* filtered

** both filtered and unfiltered

*** See appendix for target list and detection limits

Metals Detection Limit Summary

Parameter	MDL (ug/L)
Mercury	0.2
Antimony	0.5
Arsenic	0.5
Beryllium	0.2
Cadmium	0.1
Chromium	0.4
Copper	0.4
Lead	0.2
Nickel	0.3
Selenium	1.5
Silver	0.2
Thallium	0.2
Zinc	0.5
Hardness	0.2 mg CaCO ₃ /L

USGS Schedule 2010 Target Pesticides List for Water Analyses

Analyte	Method Detection Limit	Analyte	Method Detection Limit
	(µg/L, ppb)		(µg/L, ppb)
acetochlor	0.002	malathion	0.005
alachlor	0.002	metolachlor	0.002
atrazine, desethyl-	0.002	metribuzin	0.004
atrazine	0.001	molinate	0.004
azinphos-methyl	0.001	napropamide	0.003
benfluralin	0.002	parathion, ethyl-	0.004
butylate	0.002	parathion, methyl	0.006
carbaryl	0.003	pebulate	0.004
carbofuran	0.003	pendimethalin	0.004
chlorpyrifos	0.004	permethrin, cis	0.005
cyanazine	0.004	phorate	0.002
DCPA (Dacthal)	0.002	pronamide	0.003
4,4' -DDE	0.006	prometon	0.018
diazinon	0.002	propachlor	0.007
dieldrin	0.001	propanil	0.004
2,6-diethylaniline	0.003	propargite	0.013
dusulfoton	0.017	simazine	0.005
EPTC (Eptam)	0.002	thiobencarb	0.002
ethalfluralin	0.004	tebuthiuron	0.010
ethoprop	0.003	terbacil	0.007
fonofos	0.003	terbufos	0.013
alpha-BHC	0.002	triallate	0.001
gamma-BHC (Lindane)	0.004	trifluralin	0.002
linuron	0.002		

WSPMP Target Pesticides List for Water Analyses

Chlorinated Pesticides

Analyte	Quantitation Limit	Analyte	Quantitation Limit
	(µg/L, ppb)		(µg/L, ppb)
4,4'-DDT	0.035	cis-nonachlor	0.035
4,4'-DDE	0.035	trans-nonachlor	0.035
4,4'-DDD	0.035	oxychlordane	0.035
2,4'-DDT	0.035	dicosol (keithane)	0.17
2,4'-DDE	0.035	dieldrin	0.035
2,4'-DDD	0.035	endosulfan I	0.035
DDMU	0.035	endosulfan II	0.035
aldrin	0.035	endosulfan sulfate	0.035
alpha-BHC	0.035	endrin	0.035
beta-BHC	0.035	endrin aldehyde	0.035
delta-BHC	0.035	endrin ketone	0.035
gamma-BHC (Lindane)	0.035	heptachlor	0.035
captan	0.14	heptachlor epoxide	0.035
captafol	0.21	methoxychlor	0.035
cis-chlordane	0.035	mirex	0.035
trans-chlordane	0.035	pentachloroanisole	0.035
alpha-chlordene	0.043	toxaphene	0.85
gamma-chlordene	0.035		

Quantitation limits are approximate and are often different for each sample; these values are representative of a typical sample

Organophosphorus Pesticides

Analyte	Quantitation Limit	Analyte	Quantitation Limit
	(ug/L, ppb)		(ug/L, ppb)
azinphos-ethyl	0.12	fensulfothion	0.075
azinphos-methyl	0.12	fenthion	0.055
carbophenothion	0.80	fonophos	0.045
chlorpyrifos	0.055	imidan	0.080
chlorpyrifos-methyl	0.050	malathion	0.060
coumaphos	0.090	merphos	0.12
DEF	0.11	methamidophos	0.30
demeton-O	0.055	mevinphos	0.075
demeton-S	0.060	paraoxon-methyl	0.15
diazinon	0.060	parathion	0.06
dichlorvos	0.060	parathion-methyl	0.055
dimethoate	0.060	phorate	0.055
dioxathion	0.12	phosphamidan	0.18
disulfoton	0.045	propetamphos	0.15
EPN	0.075	ronnel	0.055
ethion	0.055	sulfotepp	0.045
ethoprop	0.060	suiprophos	0.055
fenamiphos	0.12	temephos	0.70
fenitrothion	0.055	tetrachlorvinphos	0.15

Chlorinated Herbicides

Analyte	Quantitation Limit	Analyte	Quantitation Limit
	(ug/L, ppb)		(ug/L, ppb)
2,4-D	0.042	bromoxynil	0.042
2,4-DB	0.050	DCPA (Dacthal)	0.033
2,4,5-T	0.033	dicamba	0.042
2,4,5-TB	0.038	dichlorprop	0.046
2,4,5-TP (Silvex)	0.033	diclofop-methyl	0.063
2,3,4,5 -tetrachlorophenol	0.023	dinoseb	0.063
2,3,4,6-tetrachlorophenol	0.023	ioxynil	0.042
2,4,5-trichlorophenol	0.025	MCPA	0.083
2,4,6-trichlorophenol	0.025	MCPP	0.083
3,5-dichlorobenzoic acid	0.042	pentachlorophenol	0.021
4-nitrophenol	0.073	picloram	0.042
acifluorfen	0.17	trichlopyr	0.035
bentazon	0.063		

Quantitation limits are approximate and are often different for each sample; these values are representative of a typical sample

Nitrogen-Containing Pesticides

Analyte	Quantitation Limit	Analyte	Quantitation Limit
	(µg/L, ppb)		(µg/L, ppb)
alachlor	0.26	metolachlor	0.28
ametryn	0.071	metribuzin	0.071
atra ton	0.21	MGK-264	0.50
atrazine	0.071	molinate	0.14
benefin	0.11	napropamide	0.21
bromacil	0.28	norflurazon	0.14
butachlor	0.25	oxyfluorfen	0.28
butylate	0.14	pebulate	0.14
carboxin	0.78	pendimethalin	0.11
chlorothalonil	0.17	profluralin	0.17
chlorpropham	0.28	prometon	0.071
cyanazine	0.11	prometryn	0.071
cycloate	0.14	pronamide	0.28
diallate	0.27	propachlor	0.17
dichlobenil	0.16	propazine	0.071
diphenarnid	0.21	simazine	0.072
diuron	0.48	tebuthiuron	0.11
eptam	0.14	terbacil	0.21
ethalfluralin	0.11	terbutryn	0.071
fenarimol	0.21	triadimefon	0.18
hexazinone	0.11	triallate	0.18
metalaxyl	0.48	trifluralin	0.11
		vernolate	0.14

Quantitation limits are approximate and are often different for each sample; these values are representative of a typical sample

BNA Analysis Detection Limit Summary

Parameter	MDL (ug/L)
1,2,4-Trichlorobenzene	0.28
1,2-Dichlorobenzene	0.28
1,2-Diphenylhydrazine	0.94
1,3-Dichlorobenzene	0.28
1,4-Dichlorobenzene	0.28
2,4,5-Trichlorophenol	1.9
2,4,6-Trichlorophenol	1.9
2,4-Dichlorophenol	0.47
2,4-Dimethylphenol	0.47
2,4-Dinitrophenol	0.94
2,4-Dinitrotoluene	0.19
2,6-Dinitrotoluene	0.19
2-Chloronaphthalene	0.28
2-Chlorophenol	0.94
2-Methylnaphthalene	0.75
2-Methylphenol	0.47
2-Nitroaniline	1.9
2-Nitrophenol	0.47
3,3'-Dichlorobenzidine	0.47
3-Nitroaniline	1.9
4,6-Dinitro-O-Cresol	0.94
4-Bromophenyl Phenyl Ether	0.19
4-Chloro-3-Methylphenol	0.94
4-Chloroaniline	0.94
4-Chlorophenyl Phenyl Ether	0.28
4-Methylphenol	0.47
4-Nitroaniline	1.9
4-Nitrophenol	0.94
Acenaphthene	0.19
Acenaphthylene	0.28
Aniline	0.94
Anthracene	0.28
Benzidine	11
Benzo(a)anthracene	0.28
Benzo(a)pyrene	0.47
Benzo(b)fluoranthene	0.75
Benzo(g,h,i)perylene	0.47
Benzo(k)fluoranthene	0.75
Benzoic Acid	1.9
Benzyl Alcohol	0.47
Benzyl Butyl Phthalate	0.28
Bis(2-Chloroethoxy)Methane	0.47
Bis(2-Chloroethyl)Ether	0.28
Bis(2-Chloroisopropyl)Ether	0.94
Bis(2-Ethylhexyl)Phthalate	0.28

APPENDIX A: Small Streams Toxicity Study Sampling and Analysis Plan

Parameter	MDL (ug/L)
Caffeine	0.094
Carbazole	0.47
Chrysene	0.28
Coprostanol	4.7
Dibenzo(a,h)anthracene	0.75
Dibenzofuran	0.47
Diethyl Phthalate	0.47
Dimethyl Phthalate	0.19
Di-N-Butyl Phthalate	0.47
Di-N-Octyl Phthalate	0.28
Fluoranthene	0.28
Fluorene	0.28
Hexachlorobenzene	0.28
Hexachlorobutadiene	0.47
Hexachlorocyclopentadiene	0.47
Hexachloroethane	0.47
Indeno(1,2,3-Cd)Pyrene	0.47
Isophorone	0.47
Naphthalene	0.75
Nitrobenzene	0.47
N-Nitrosodimethylamine	1.9
N-Nitrosodi-N-Propylamine	0.47
N-Nitrosodiphenylamine	0.47
Pentachlorophenol	0.47
Phenanthrene	0.28
Phenol	1.9
Pyrene	0.28

Chronic Toxicity Tests

While laboratory analytical procedures are not normally included in a Sampling and Analysis Plan, toxicity testing for the 1999 Small Streams Toxicity Study are innovative enough to be included here.

Sample Treatment:

Upon arrival to the laboratory the following water quality parameters will be measured in each 6-L sample from the test and reference sites: temperature, dissolved oxygen, pH, total alkalinity, total hardness and conductivity. Half the volume of each sample will be filtered through a 0.45 μm Gelman mini capsule filter and the samples will be refrigerated at $4 \pm 2^\circ\text{C}$ until use. Samples will be mixed before filtering.

The two chronic toxicity tests *Ceriodaphnia dubia* and *Selenastrum capricornutum* will be performed on all the samples collected at the 3-4 sites during the four sampling events (spring runoff, summer base flow, early fall runoff, and late fall runoff). The tests will be initiated within 24 hours of the samples arriving to the laboratory within 36 hours of collection, whatever is sooner.

Water Flea - *Ceriodaphnia dubia* (7-Day Chronic Toxicity Test)

The *C. dubia* chronic toxicity test will be conducted as outlined in Lewis *et al.* (1994). The undiluted, unfiltered (100%) samples will be tested along with the undiluted, filtered (100%) samples and a 0% filtered and unfiltered sample (Lake Washington water only). Ten replicates containing one organism each will be tested at each treatment. Each test chamber will contain 15 mL of solution in a 30-mL plastic cup. Test organisms will be neonates (< 24h old) taken from an overnight brood board composed of adults isolated from in-house mass cultures. Individual broods will be blocked across treatments with each replicate representing a different brood. One replicate will be assigned per row of the test chamber, and then treatments will be randomized within each row. The test will be incubated for 7 days at $25 \pm 1^\circ\text{C}$ on a 16:8 hour light:dark cycle. Solutions will be renewed and animals fed daily. Reproduction, mortality, and water quality measurements will be recorded every 24 hours at the time of solution renewal. Monthly reference toxicant test with cadmium will be used to assess the health of the organisms.

Green Algae - *Selenastrum capricornutum* (96-Hour Chronic Toxicity Test)

The *S. capricornutum* chronic toxicity test will be conducted as outlined in Lewis *et al.* (1994). Briefly, nutrients (including EDTA) equivalent to those in the culture water (algal assay medium, or "AAM") will be added to both the filtered (0.45 μm) and unfiltered samples in order to ensure that toxicity is not confused with a lack of nutrients. The filtered and unfiltered samples will be tested along with a 0% filtered and unfiltered dilution medium sample (AAM only). Each treatment will be tested with four replicates. Each replicate will consist of 50 mL of solution added to a 125 mL sterile flask covered with an inverted beaker and inoculated with 1 mL at a concentration of 51×10^4 cells/mL, resulting in an initial density of 1.03×10^4 cells/mL. The flasks will be incubated for 96 hours at $25 \pm 1^\circ\text{C}$ under constant light (3,780 - 3,880 lux) in a pattern determined by random number assignment. Twice daily the flasks will be mixed and the positions in the

incubator rotated. Temperature will be measured daily in the incubator and pH will be measured in each treatment at test initiation and termination. After 96 hours of exposure the algae growth in each flask is measured by cell counts. Concurrent reference toxicant test with sodium chloride will be used to assess the growth of the algae.

Data Analysis

The *C. dubia* survival data from each test site will be compared with the survival data from the reference site based on treatment (100% filtered and 100% unfiltered). In addition, the survival data between the two treatments from each site will be compared. The statistical analysis will be performed using a Chi-square test. The reproduction data from each test site will be compared with the reproduction data from the reference site based on treatment (100% filtered and 100% unfiltered). In addition, the reproduction data between the two treatments from each site will be compared. The statistical analysis will be performed using a t-test or a Wilcoxon rank sum test depending on the normality and homogeneity of the data. The normality and homogeneity of the data will be analyzed using a Shapiro Wilk test and an F-test. Overall test acceptability is based on the survival and reproduction data from the 0% unfiltered Lake Washington sample. The filtered Lake Washington sample will be compared with the unfiltered sample to determine whether filtration had an effect. The statistical analyses will be as listed above. Reference toxicant data will be compared to the control chart and precision table to ensure that the reproduction data (IC25) falls within the control limits (± 2 times standard deviation).

The *S. capricornutum* growth data from each test site will be compared with the growth data from the reference site based on treatment (100% filtered and 100% unfiltered). In addition, the growth data between the two treatments from each site will be compared. The statistical analysis will be performed using a t-test or a Wilcoxon rank sum test depending on the normality and homogeneity of the data. The normality and homogeneity of the data will be analyzed using a Shapiro Wilk test and an F-test. Overall test acceptability is based on the growth data from the 0% unfiltered dilution medium sample (AAM only). The filtered dilution medium sample will be compared with the unfiltered sample to determine if filtration had an effect. The statistical analyses will be as listed above. Reference toxicant data will be compared to the control chart and precision table to ensure that the growth data (EC50) falls within the control limits (± 2 times standard deviation).

Data Reporting

All data are to be reported within 45 days of sample receipt. Data are to be reported to Dean Wilson of King County.

The following information is to be reported for all chemistry data: analyte, CAS number (if applicable), detection limit, result, date prepared, date analyzed, method used, and definition of any qualifiers. Surrogates percent recoveries for all organic methods. Data are to be reported in an electronic EXCEL spreadsheet format along with the laboratories standard hard copy report.

Laboratory standard QC are to be reported along with sample data.

Data are to be reported in standard reporting format for toxicity testing. All water quality values will also be reported from the toxicity studies.